

REPORT NO. NADC-85029-80 ✓

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## CORROSION-PREVENTIVE PRIMERS FOR MILITARY EQUIPMENT

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1 APRIL 1985

FINAL REPORT  
AIRTASK NO. AIR-310-310A/001B/4F61-542-000  
Work Unit ZM540

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Prepared for  
NAVAL AIR SYSTEMS COMMAND  
Department of the Navy  
Washington, DC 20361

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS N/A	
2a. SECURITY CLASSIFICATION AUTHORITY N/A		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for Public Release; Distribution Unlimited	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE N/A			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) NADC-85029-60		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION Aircraft and Crew Systems Technology Directorate	6b. OFFICE SYMBOL (if applicable) 6062	7a. NAME OF MONITORING ORGANIZATION	
6c. ADDRESS (City, State, and ZIP Code) NAVAL AIR DEVELOPMENT CENTER Warminster, PA 18974		7b. ADDRESS (City, State, and ZIP Code)	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Naval Air Systems Command	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code) Department of the Navy Washington, DC		10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. PROJECT NO. TASK AIR-310 NO 310A/0018/ WORK UNIT 4F61-542-000 ZM540	
11. TITLE (Include Security Classification) CORROSION-PREVENTIVE PRIMERS FOR MILITARY EQUIPMENT			
12. PERSONAL AUTHOR(S) Stephen J. Spadafora, Charles R. Hegedus, and David F. Pulley			
13a. TYPE OF REPORT Final	13b. TIME COVERED FROM TO	14. DATE OF REPORT (Year, Month, Day) 1985 April 1	15. PAGE COUNT 29
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES FIELD GROUP SUB-GROUP		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Organic Coatings Corrosion Protection Military Equipment	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The operational readiness and life-time of military equipment can be significantly reduced by corrosion. One way of protecting equipment against this process is through the use of corrosion-preventive primers. These primers are composed of a variety of resins, pigments and solvents to produce materials with different properties to cover a broad range of operational environments.  Eleven primers conforming to military and federal specifications were tested on steel and aluminum specimens. Properties such as corrosion protection, adhesion, flexibility and chemical resistance were determined for each primer. The results of this evaluation indicate a wide variety of performance properties for the eleven primers. This information is presented to enable the reader to choose a material with the most appropriate properties for a specific use.  <i>Additional keywords: organic coatings; drying time; corrosion resistance; fluid resistance; volatile organic compound content.</i>			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

**SECURITY CLASSIFICATION OF THIS PAGE**

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## INTRODUCTION

Corrosion is a major reason for the high cost of maintaining and repairing military equipment. It can be minimized through the application of corrosion-inhibiting primers to all metallic substrates before topcoating. These primers contain reactive pigments such as chromates, phosphates, oxides, etc. that help to passivate metals and neutralize aggressive ions at the primer/metal interface. Many military specifications have been written for the procurement of these materials. Eleven of the more common specifications are given in Table 1. They differ in regard to composition and intended application. This information can be obtained from the specifications. Table 2 lists the binder, resin, and solvent systems of these materials. The purpose of the study is to give those who specify and apply such materials a guide to their comparative performance and limitations. For each specification, a single primer was obtained directly from a qualified manufacturer. Their names and product numbers have been withheld from this report, since it is not our intent to endorse any proprietary formulation. The selection of a primer for a particular application should be based on many factors including cost, performance, intended use, and environmental conditions. The optimum material for one application may not be adequate for another. We hope that this report will make the task of choosing the proper material somewhat easier.

## PROCEDURE

With the exception of flexibility and filiform corrosion, all of the test properties were conducted on 1010 carbon steel and 2024T3 aluminum alloy. The steel panels were pretreated with a zinc phosphate coating in accordance with specification DOD-P-16232. The aluminum panels were pretreated with a chromate conversion coating in accordance with specification MIL-C-5541 using materials conforming to specification MIL-C-81706. The flexibility tests were conducted on 2024-0 aluminum alloy (annealed) that was anodized in accordance with specification MIL-A-8625, Type II. Filiform corrosion was performed on Alclad 2024-T3 aluminum alloy panels which were pretreated with the above chromate conversion coating. The primers were mixed as prescribed by the manufacturer and applied by conventional air spray to a dry-film thickness of 1.0 to 1.5 mils. They were then cured for seven days at room temperature before testing. The physical properties of each primer were determined in accordance with test methods from the American Society for Testing and Materials (ASTM) and Federal Test Method Standard (FTMS) No. 141B.

## DRYING TIME (ASTM D1640)

The tack-free time is defined as the period of time from application until no tackiness is evident to the touch. At this point, the primer is ready for topcoating. The dry-hard time is defined as the period of time from application until the film cannot be permanently marred using firm thumb pressure. At this point, items that receive only a coat of primer are now ready to be handled.

## ADHESION (ASTM D3359, ASTM D2197)

After 24 hours of water immersion, the crosshatch instrument was used to scribe 11 parallel lines (1 mm apart) through the film and again in a perpendicular direction, so that a grid of 100 squares was formed. A strip of 3M-250 masking tape was then applied over the grid with firm thumb pressure and removed with one quick motion. Standards for evaluation of adhesion, based on the area of primer removed, are given in the test method. Another means of determining adhesion was the Arco Microknife. With this method, parallel cuts were made in the film through to the substrate. These cuts were made closer and closer together until the primer between the cuts was sheared from the panel. The adhesion rating was calculated from a formula that included the shearing force as a variable.



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**TABLE 1. MATERIALS LIST**

<u>Specification</u>	<u>Title</u>
TT-P-664	Primer Coating, Synthetic, Rust-inhibiting, Lacquer-resistant
TT-P-1757	Primer Coating, Zinc Chromate, Low Moisture Sensitivity
MIL-P-23377	Primer Coatings, Epoxy-polyamide, Chemical and Solvent Resistant
MIL-P-26915	Primer Coating, Zinc Dust Pigmented, for Steel Surfaces
MIL-P-52192	Primer Coating, Epoxy
MIL-P-52995	Primer Coating, Synthetic, Corrosion-inhibiting, Lacquer-resisting, Lead and Chromate-Free
MIL-P-53022	Primer Coating, Epoxy, Corrosion-inhibiting, Lead and Chromate-Free
MIL-P-53030	Primer Coating, Epoxy, Water Reducible, Lead and Chromate-Free
MIL-P-85582	Primer Coatings, Epoxy, VOC Compliant, Chemical and Solvent Resistant
MIL-P-87112	Primer Coating, Elastomeric, Polysulfide, Corrosion-inhibiting
MIL-P-XXXXX*	Primer Coatings, Polyurethane, Elastomeric, Corrosion-inhibiting

\*One-component, Polyurethane Primer

TABLE 2. COMPONENTS OF THE PRIMERS EVALUATED

<u>Specification</u>	<u>Binder</u>	<u>Corrosion-Inhibiting Pigments</u>	<u>Solvent</u>
TT-P-664	Phthalic Alkyd	Iron Oxide, Zinc Chromate	Organic
TT-P-1757	Phthalic Alkyd	Zinc Chromate	Organic
MIL-P-23377	Epoxy	Strontium Chromate	Organic
MIL-P-26915	Epoxy	Zinc	Organic
MIL-P-52192	Epoxy	Iron Oxide, Basic Lead-Silica Chromates	Organic
MIL-P-52995	Phthalic Alkyd	Iron Oxide, Zinc Phosphate, Organo-Zinc Salt	Organic
MIL-P-53022	Epoxy	Zinc Phosphate, Organo- Zinc Salt	Organic
MIL-P-53030	Epoxy	Iron Oxide, Zinc Phosphate, Organo-Zinc Salt	Water/Organic
MIL-P-85582	Epoxy	Barium Chromate	Water/Organic
MIL-P-87112	Polysulfide	Chromates	Organic
MIL-P-XXXXX	Polyurethane	Zinc Chromate	Organic

#### FLEXIBILITY (FTMS 6226, ASTM D2794, ASTM D1737)

The impact resistance of the primer was measured with both the GE and Gardner instruments. The results are given as the maximum percentage elongation (GE) or inch-pounds of energy (Gardner) that the primer can withstand without cracking. Mandrel-bend tests were conducted over 1/8, 1/4, 1/2, and 1" mandrels. This test was performed at a temperature of -60°F. The smallest mandrel around which the coated panel could be bent without cracking was recorded.

#### CORROSION RESISTANCE (ASTM B117, ASTM G85, ASTM D2803)

Four sets of primed steel and aluminum panels were scribed in a figure "X" down to bare metal and mounted in 15° racks. Two sets were exposed in a 5% salt-spray cabinet for 1000 hours. Another two sets were exposed in a SO<sub>2</sub>/salt-spray cabinet for 400 hours. The panels were then observed for undercutting at the edge of the scribe lines and blistering over the rest of the panel. Filiform tests were conducted only on scribed Alclad aluminum panels that were primed and topcoated with MIL-C-83286 polyurethane topcoat. Two panels for each primer were exposed to 12 N hydrochloric acid vapors for one hour to initiate the corrosion process. Then the panels were thoroughly rinsed with distilled water and placed in a 85% R.H. humidity cabinet for 500 hours at ambient temperature. After this exposure, they were examined for filiform corrosion leading from the scribe lines.

#### FLUID RESISTANCE

The fluid resistance of the primers was evaluated by exposing the coated panels to three types of fluids: hydraulic fluids, lubricating oils, and hydrocarbons. Resistance to hydraulic fluids was determined by immersing the coated panels in specification MIL-H-5606 and MIL-H-83282 hydraulic fluids for 24 hours at 150°F. The primers were then observed for softening or other signs of film degradation. Resistance to lubricating oils was ascertained by immersing the primed panels in MIL-L-23699 lubricating oil for 24 hours at 250°F. Again, the primers were evaluated for film softening or degradation. Resistance to hydrocarbons was determined by rubbing a cloth rag soaked in methyl ethyl ketone or specification MIL-T-5624, Grade JP-4 aviation fuel back and forth across the surface of the primer about ten times. Complete removal of the coating from the panel represented failure in these tests.

#### VOLATILE ORGANIC COMPOUNDS CONTENT (ASTM D3960)

The volatile organic compounds (VOC) content of each primer was determined by diluting the material with the recommended thinner to spray viscosity (18 seconds through a Zahn No. 2 cup). The volatile components were then measured, and the results were recorded as the grams of VOC per liter of paint (less water).

#### RESULTS AND DISCUSSION

The drying-time of the primers evaluated was recorded for both tack-free and dry-hard conditions. These results are listed in Table 3. Tack-free times ranged from 15 minutes to three hours with the majority of materials becoming tack-free in 30 to 45 minutes. Drying-time is a property usually considered during equipment processing. The tack-free time for a primer is generally the minimum period after application before the material can be overcoated with either a sealant or topcoat. If the equipment being painted is occupying valuable space in a spray-booth or hangar, shorter tack-free times are desirable.

The dry-hard time is generally the minimum period after application before equipment can be handled without risk of easily damaging the coating. The materials tested had dry-hard times ranging

TABLE 3. TEST RESULTS

Drying Time (Hou.s)		Adhesion Tests				Flexibility Tests				Hydraulic Fluids	Lubricating Oil	Solvent Resistance	Fuel	Spray Viscosity
		Crosshatch (Wet)		Microknife		IMPACT								
		Best: Worst	Adhesion Value	G.E.	Gardner (in. lbs.)	Mandrel Bend (Inch)								
Tack Free	Dry Hard	AL	ST	AL	ST	%	Direct	Reverse	MIL-H-5606 and MIL-H-83282 150°F	MIL-L-22599 (250°F)	MEK	JP-4 Resistance	VOC Gm/l	
		58	58	1.2	2.1	20	120	110						1/8
		58	58	2.4	2.7	1.0	10	40						1/2
		58	58	1.3	2.6	1.0	40	40						1/4
		58	58	2.0	1.6	0.5	40	40						>1
		58	58	2.5	1.9	20	20	20						1/4
		58	58	1.7	2.7	10	30	40						1/8
		58	58	1.5	2.3	10	30	10						1/2
		58	58	2.1	2.7	20	60	30						1/8
		58	58	1.7	2.3	20	60	80						1/8
3.0		>8	58	58	3.8	--	40	>160	>160	1/8"	P	P	532	
One Component Urethane Primer		1.0	2.0	58	58	2.2	3.0	60	>160	>160	1/8	P	P	790

P - Pass    S - Softened    R - Removed    SR - Slight Removal

from 30 minutes for TT-P-664 to eight hours for MIL-P-97112. Most coatings were dry-hard in two to four hours. If critical space and time are being wasted while waiting for a primer to dry, a material with a quicker cure is desirable. For example, at many rework facilities, aircraft are stripped of all paints, and corrosion is removed. The aircraft is then cleaned, and a fresh coat of primer is applied for corrosion protection during the rework process (which may last several months). The next step in the process cannot begin until the primer is dry-hard in order to minimize possible damage to the coating.

Adhesion of the primer to military equipment is of great importance. This is especially true when considering the operational environment of the equipment. In many cases, the climate is harsh and demanding (such as on aircraft carrier). Also, the conditions of use are severe. Army and Marine Corps vehicles may be driven off the road through dirt and water. When not in operation, they are frequently walked on or scraped by tools causing mechanical damage to the coating. In areas where the coating has been chipped, the underlying metal is exposed to the environment, and the corrosion process is initiated. Therefore, a durable and adherent film is necessary.

Adhesion was measured by the wet cross-hatch and microknife methods. The results of these tests are listed in Table 3. Cross-hatch results for all primers on the aluminum specimens was 5B, which indicates excellent adhesion. On steel specimens, all primers exhibited 5B adhesion except MIL-P-85582 and MIL-P-53022 (2B) and MIL-P-23377D (3B). Figure 1 illustrates that the latter results are only fair in comparison to a 5B rating. It must also be considered that this test was performed after 24 hours of immersion in water. Therefore, it was influenced by the water resistance of the primers.

Microknife adhesion results ranged from 1.6 to 3.0 on steel and 1.2 to 3.8 on aluminum (the lower numbers indicate better adhesion). This test was performed at ambient conditions. There is no correlation between these and the cross-hatch results. However, the cross-hatch results showed no difference between many of the coatings, while the microknife results indicated fine differences in the adhesive strength of the primers tested. For instance, TT-P-664 and MIL-P-52192 both had a 5B adhesion on aluminum; but TT-P-664 yielded 1.2 in the microknife, and MIL-P-52192 yielded a 2.5, indicating that the former is more adherent. Cross-hatch and microknife results are empirical and should only be used as an indication of the trend of adhesive strengths of the primers tested.

The impact flexibility of the primers on O-temper, aluminum specimens was measured at ambient conditions by two methods: the GE impact test and the Gardner test. The GE impact test indicates the maximum elongation of the coating before cracking occurs. The Gardner test yields the highest impact energy applied to the specimen before the coating cracks. The results of these tests are presented in Table 3. The GE results range from 0.5% for MIL-P-26915 to 60% for the one component, urethane coating. The Gardner results range from 10 inch-pounds to greater than 160 inch-pounds. These results, in some cases, are lower than specified requirements. This is suspected to be due to the surface characteristics of the specimens. However, all of the primers were applied to the same batch of specimens, and the results can be used on a comparative basis. Figure 2 is a graph comparing the results from the two tests. This graph shows some agreement between the two methods. However, there is more variation in the Gardner results. For instance, there are four primers which have a GE impact of 20% elongation; but the Gardner results on these materials range from 20 to 110 in-lbs, showing a differentiation between materials.

Impact flexibility is necessary if a coating is on a substrate which is often flexed or impacted. As previously mentioned, ground vehicles are frequently impacted with tools and other hard objects. This property indicates the likelihood of the protective coating being damaged by rough handling.

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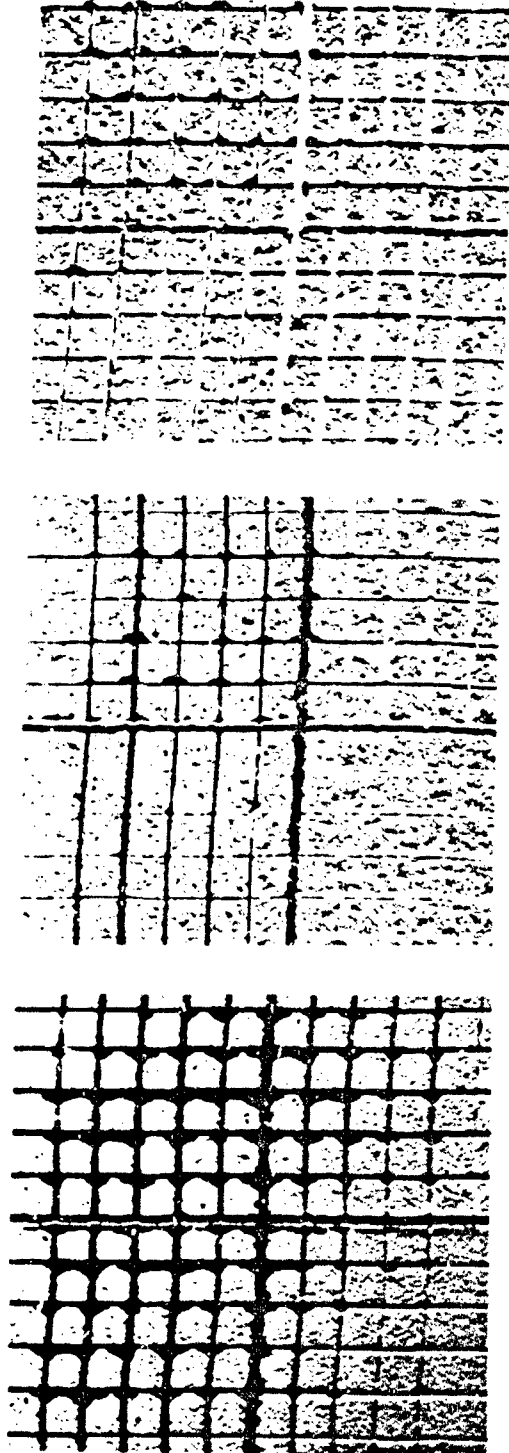


Figure 1. Comparison of Cross Hatch Test Results

**Figure 2. G.E. Versus Gardner Impact Test Results**

Low-temperature (-60°F) flexibility was measured by performing a 180 degree bend over 1/8, 1/4, 1/2, and 1 inch mandrels with primed, O-temper, aluminum specimens. Table 3 lists the smallest mandrel on which the coated specimen could be bent without cracking. MIL-P-26915 failed over all the mandrels. MIL-P-53022 and TT-P-1757 passed the 1/2 inch mandrel, while MIL-P-23377D passed the 1/4 inch mandrel. All other primers passed the 1/8 inch mandrel. This is an indication of how these primers will perform when exposed at low temperatures. Aircraft are exposed to such temperatures during high-altitude flight

The results for the fluid resistance tests appear in Table 3. All eleven primers passed immersion in standard aircraft hydraulic fluids (MIL-H-5606 and MIL-H-83282) at 150°F (66°C). No softening occurred on any of the panels tested, although the one-component, urethane primer and the TT-P-1757 did discolor slightly. Immersion in MIL-L-23699 lubricating oil at 250°F (121°C) softened both MIL-P-52995 and MIL-P-26915 to the point where the coatings could be removed by wiping with a cloth using slight pressure. The MIL-P-26915 was also softened in the vapor phase section of the specimen (exposed above the fluid), such that the coating could be wiped off the panel with slight pressure. Except for some discoloration, all of the other primers were unaffected by the lubricating oil.

The results for the solvent resistance test appear in Table 3. Most of the coatings exhibited good resistance to methyl ethyl ketone (MEK). However, three of the coatings (TT-P-664, MIL-P-52995, and MIL-P-52192) were softened and removed when wiped with a cloth soaked with MEK.

The results for the fuel resistance test appear in Table 3. TT-P-664 and MIL-P-52995 primers had small amounts of the coating removed when wiped with a cloth soaked in JP-4 aviation fuel. The rest of the primers were unaffected.

The fluid resistance, fuel resistance, and solvent resistance tests are designed to test the chemical resistance of a coating. Most of the primers performed well in these tests. MIL-P-52995 failed all three tests and should not be used in any area where chemical resistance is a requirement. TT-P-664 failed both fuel resistance and solvent resistance tests, and MIL-P-52192 failed the solvent resistance test. Therefore, these primers should not be used in areas around fuel tanks where they may be exposed to hydrocarbons. MIL-P-26915 failed the lubricating oil exposure in both the immersed and vapor phase and, therefore, should not be used in any area where lubricating oils are present (such as aircraft engine compartments). Any of the other primers could be used in these areas, and all of the primers evaluated could be used in areas where hydraulic fluids are present.

The volatile organic compounds (VOC) of the subject primers were measured at standard, air-spray viscosity (18 seconds through a Zahn No. 2 cup), and the results appear in Table 3. Most of the primers have a VOC in the range of 525 to 625 grams per liter. The values for MIL-P-53030 and MIL-P-85582 are 315 and 325 grams per liter, respectively. These are low because the two primers are water-borne, while the rest are solvent-borne. The one-component, urethane primer has a VOC of 780 grams per liter.

The VOC of a coating represents the amount of organic vapor emitted to the atmosphere during and after application. Since most organic vapors are hazardous to the environment, their concentration during coating application is often limited. An example of this is South Coast Air Quality Management District Rule 1142 for the Los Angeles area. Water-borne primers or exempt solvents (such as trichloroethane) must be used to meet solvent emission limitations. Where these laws do not exist, any of the primers could be used.



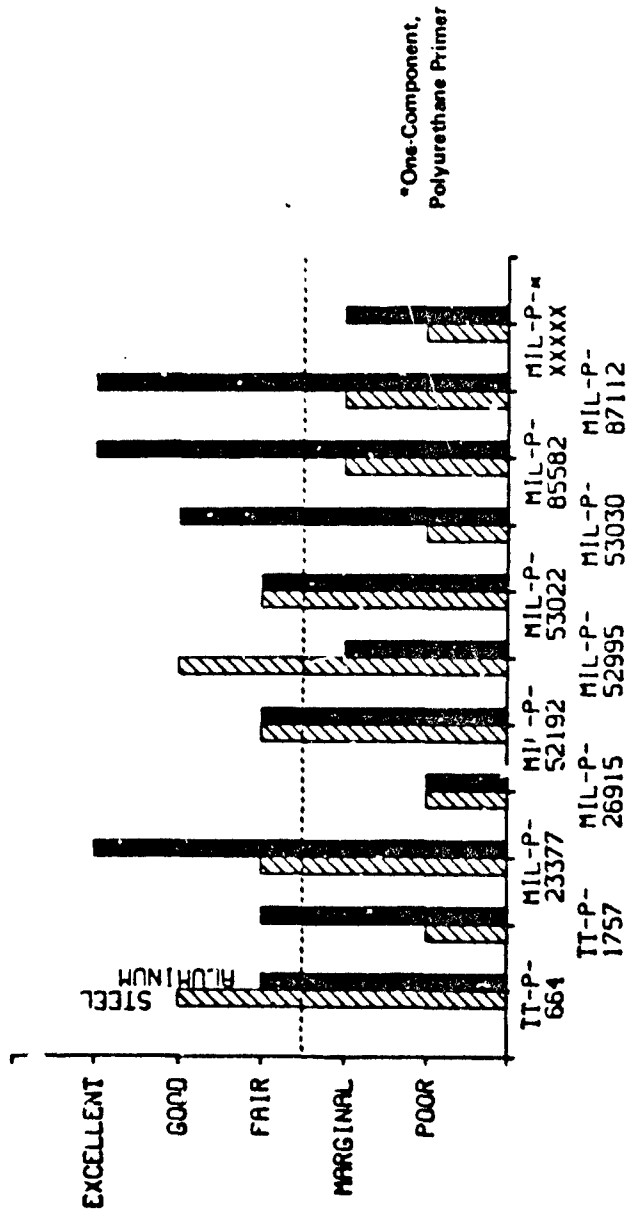
Three corrosion tests were performed during this study: 5% salt-spray, SO<sub>2</sub>/salt-spray, and filiform corrosion. Salt-spray and SO<sub>2</sub> tests were performed on both steel and aluminum. Filiform testing was performed only on aluminum. All test specimens were first inspected with the coating intact and then after the coating was chemically removed from the substrate. Similar results were observed on the coated panels and the stripped panels.

The results of the 5% salt-spray tests appear in Figure 3. Steel specimens exposed to 1000 hours of 5% salt-spray are shown in Figures 4 and 5. These results indicate that iron oxide pigment systems generally inhibit corrosion of steel better than other inhibiting systems. Strontium chromate and the zinc phosphate/organo-zinc salt systems also performed well. Coatings with just zinc or zinc chromate inhibitors performed poorly. It should be noted that the inhibitor is only one phase of the corrosion protection of a primer. The resin system provides a physical barrier against the corrosive environment. If the resin cannot withstand the environmental exposure, the coating can fail regardless of the pigment system.

Aluminum specimens exposed to 1000 hours of 5% salt-spray appear in Figures 6 (painted) and 7 (stripped). These results show that under salt-spray conditions, chromates provide the best corrosion protection for aluminum, with zinc phosphate and iron oxide systems providing fair protection. Again, this is only true if the resin system can withstand the environmental conditions. It was observed that the zinc pigmented primer (MIL-P-26915) performed well when initially exposed to the salt-spray environment. During this time, white corrosion products (probably zinc oxide) formed on the surface. After 200 hours, these products diminished, indicating a depletion of zinc. During the additional exposure period, corrosion of the substrate occurred.

The final results for the SO<sub>2</sub>/salt-spray tests on steel and aluminum specimens were taken after 400 hours of exposure. These results appear in Figure 8. Periodic evaluations of the specimens were performed throughout the test. These evaluations indicated that the specimens which showed signs of corrosion first were the most corroded specimens in the final evaluation. All of the specimens exposed had corrosion in the scribe, indicating the severity of the test conditions. The steel specimens from this test appear in Figures 9 (painted) and 10 (stripped). These results indicate that the zinc phosphate/organo-zinc salt inhibitor system and the iron oxide inhibitor provided the best protection on steel under these conditions. Chromate inhibitors again provided very little protection for steel. The aluminum specimens from the SO<sub>2</sub>/salt-spray test appear in Figures 11 (painted) and 12 (stripped). These results indicate that the zinc phosphate/organo-zinc salt inhibitor system and the iron oxide inhibitor system and the iron oxide inhibitor provided the best corrosion inhibition on aluminum. Strontium chromate and zinc inhibitors also provided fair protection on aluminum. The rest of the chromate inhibited primers, however, were not very effective in providing protection against the SO<sub>2</sub>/salt-spray environment. This can be seen dramatically with MIL-P-85582 and MIL-P-87112 primers. These materials provided excellent protection for 1000 hours of regular salt-spray, while both materials performed poorly in less than 400 hours of SO<sub>2</sub>/salt-spray exposure.

The results of the filiform corrosion test appear in Figure 13. Filiform corrosion appears as filament-shaped or threadlike corrosion products leading away from the scribe lines. This type of corrosion usually occurs in acidic and humid environments. As these corrosive conditions become more severe, the process can tend to go from filiform to other forms of localized corrosion. Figures 14 (painted) and 15 (stripped) show the filiform test specimens. These results indicate that the chromate inhibitors and zinc provided the best protection against the environment. The zinc phosphate/organo-zinc salt inhibitor system also provided fair protection.



- Excellent: No corrosion in scribe or on the rest of the panel
- Good: Some corrosion in scribe, but no corrosion on the rest of the panel
- Fair: Corrosion in scribe and a few (2-4) spots on the rest of the panel
- Marginal: Corrosion in scribe and roughly a dozen spots over the rest of the panel
- Poor: Heavy corrosion in the scribe and over the rest of the panel

Figure 3. Results for 5% NaCl Salt-Spray Tests

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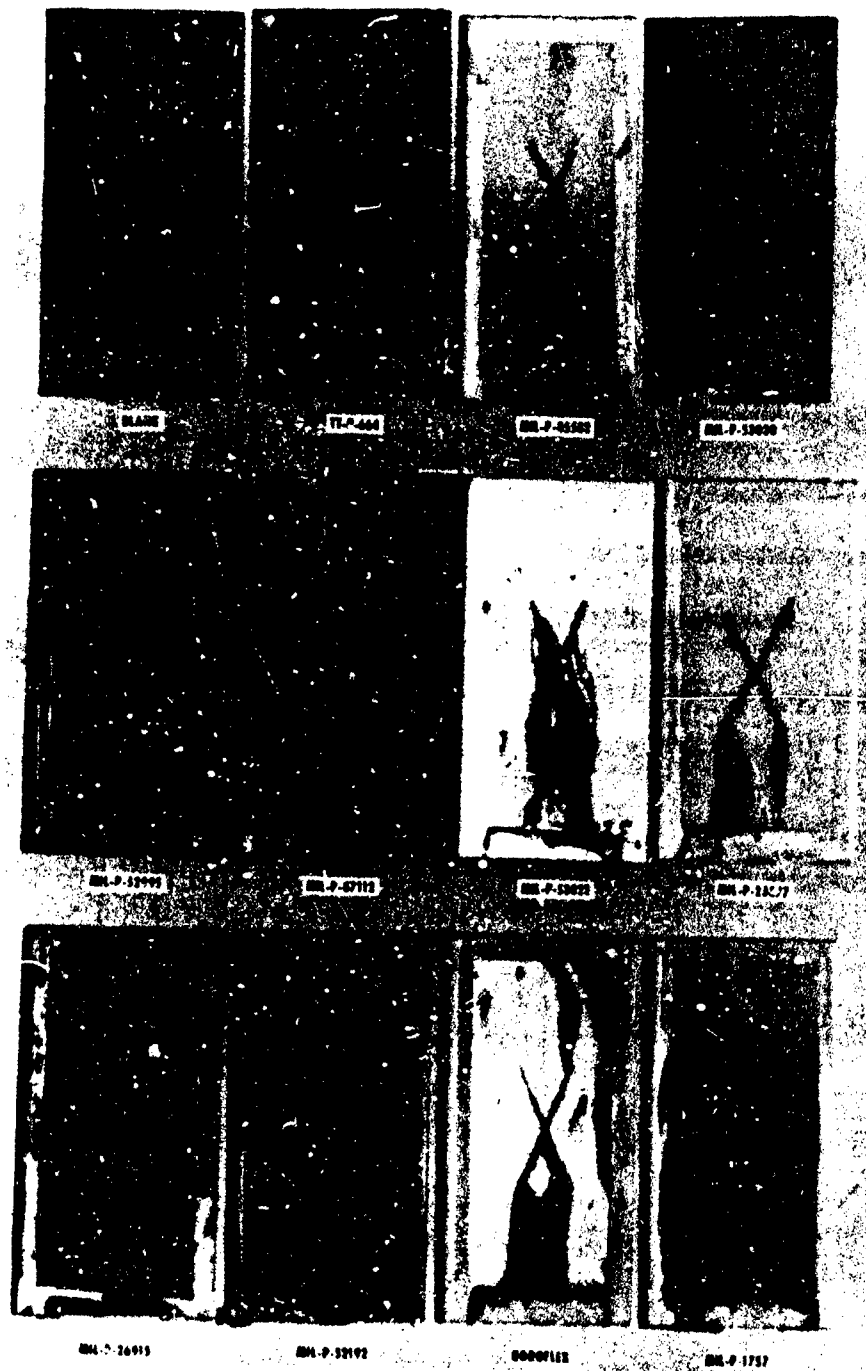


Figure 4. Steel Specimens (Painted) From 5% Salt-Spray Test

NADC-85029-60

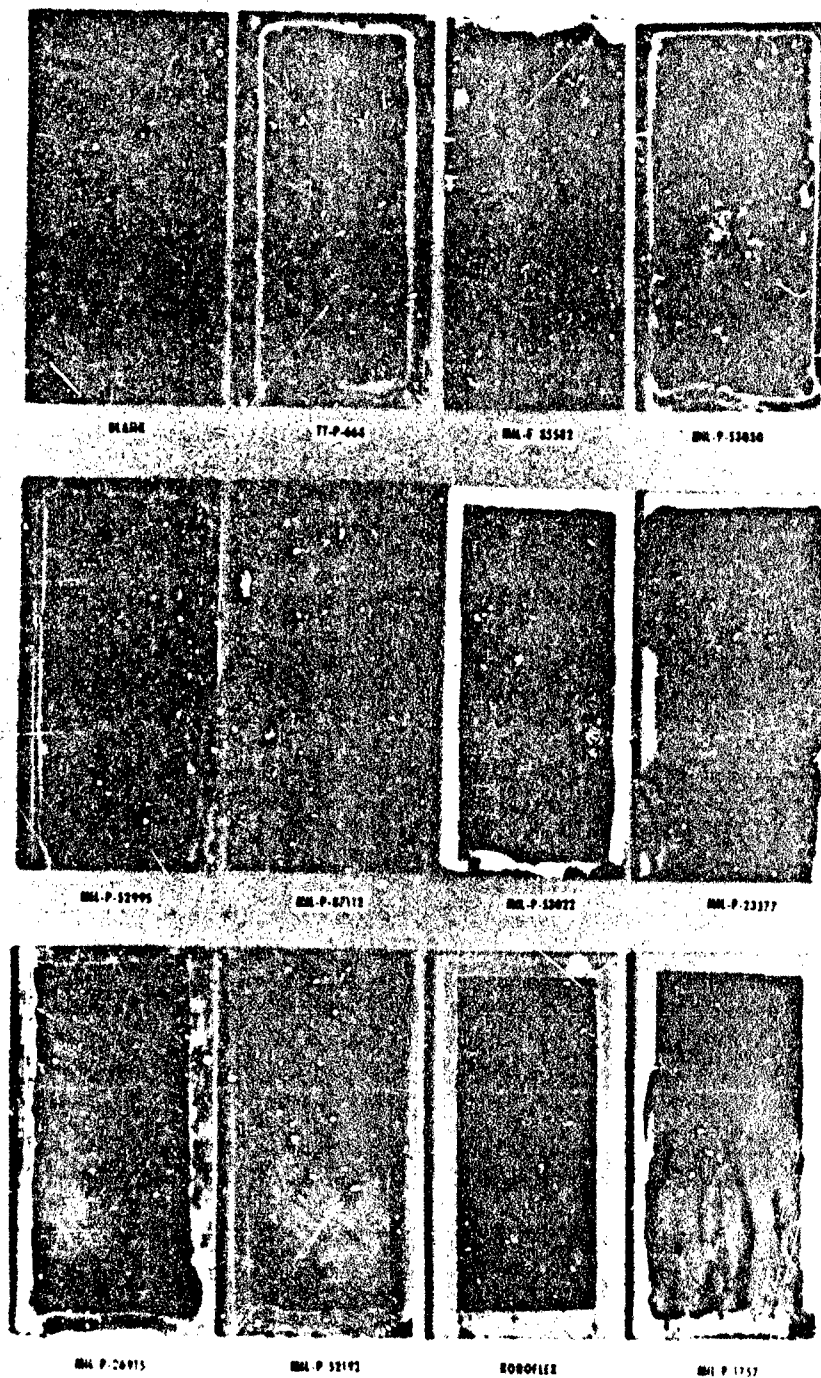


Figure 5. Steel Panels (Stripped) From 5% Salt-Spray Test

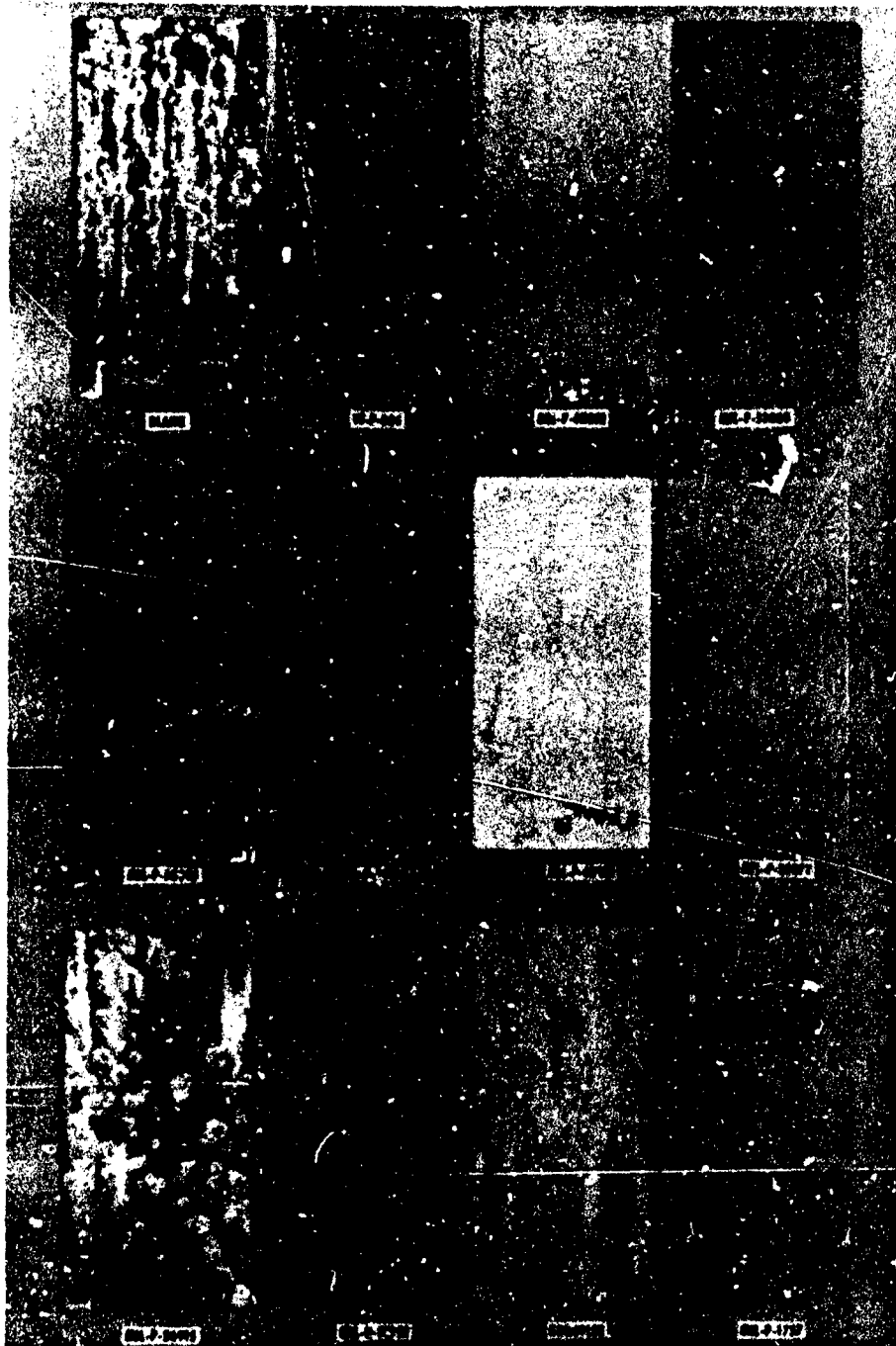


Figure 6. Aluminum Panels (Painted) From 5% Salt-Spray Test

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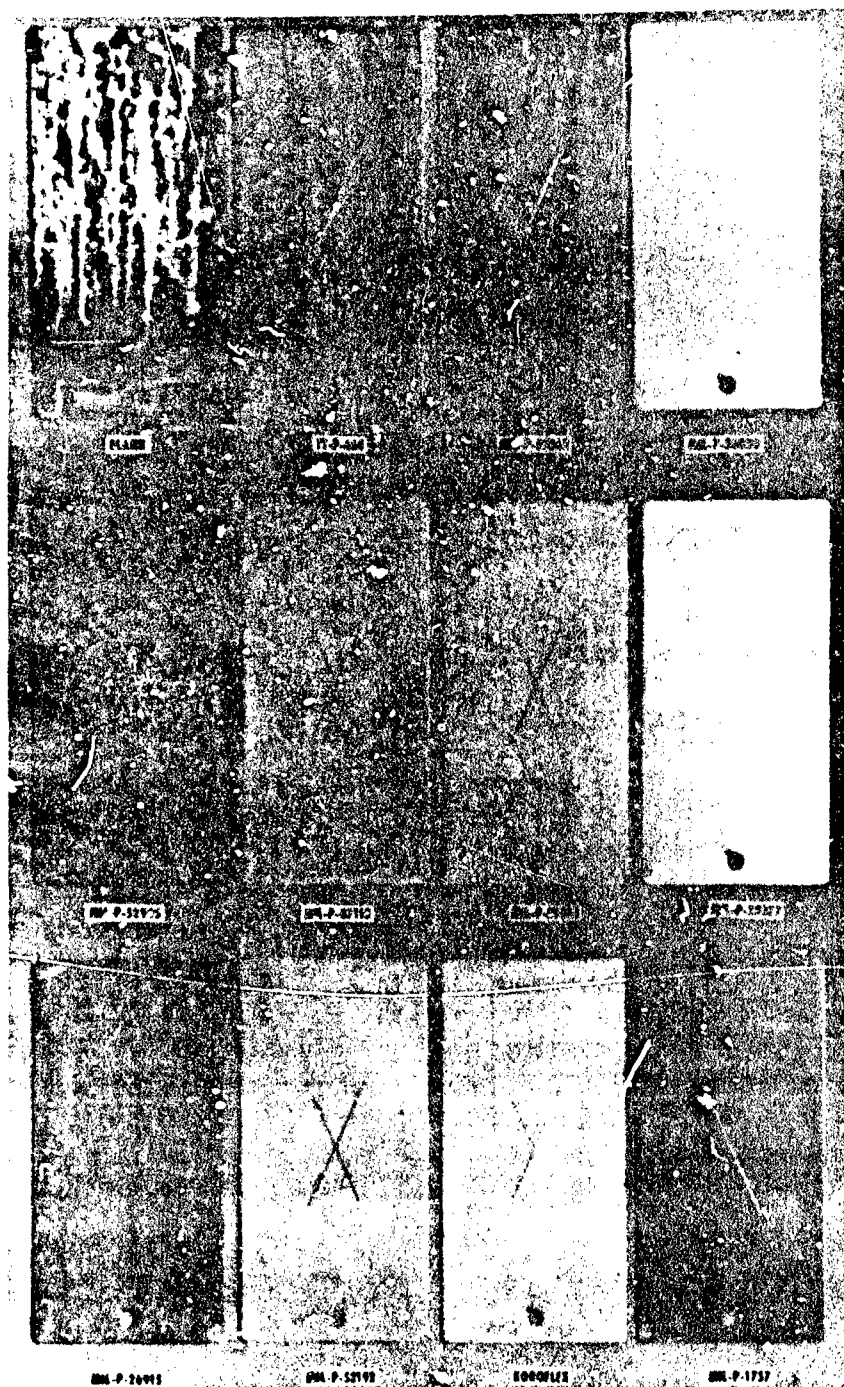
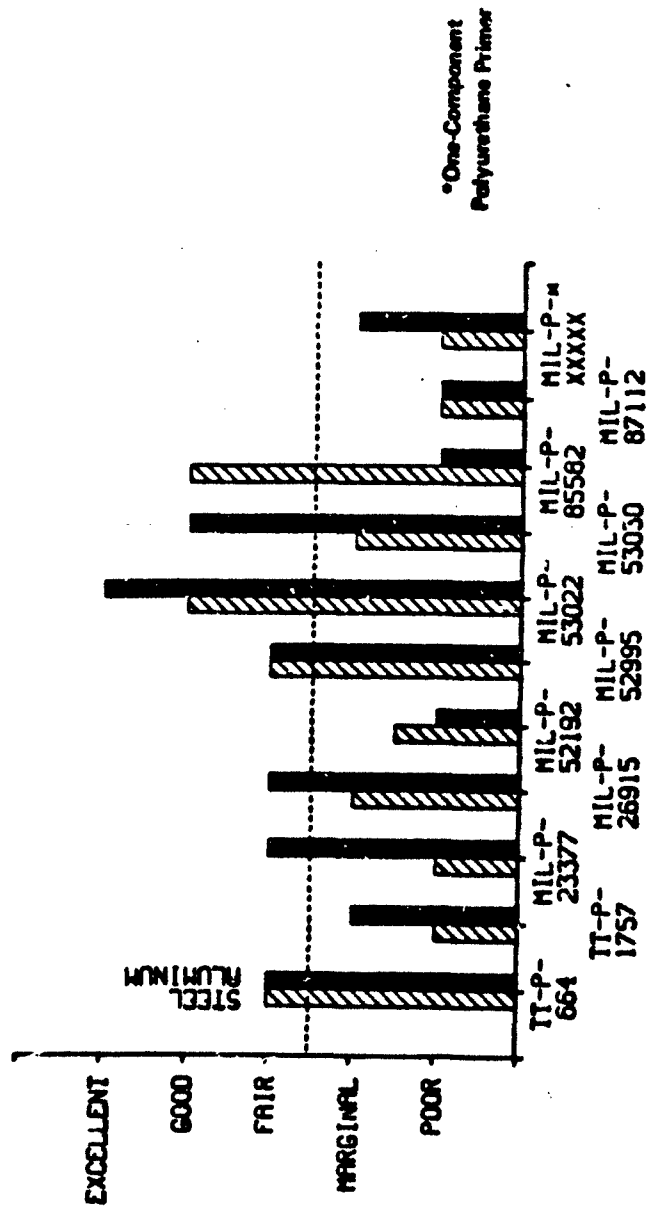


Figure 7. Aluminum Panels (Stripped) From 5% Salt-Spray Test



- Excellent:** Some corrosion in scribe, but no corrosion on the rest of the panel
- Good:** Corrosion in the scribe and on less than 10% of the rest of the panel
- Fair:** Corrosion in the scribe and over less than one-third of the panel
- Marginal:** Corrosion in the scribe and over less than two-thirds, but greater than one-third, of the panel
- Poor:** Corrosion in the scribe and over the entire surface of the panel

Figure 8. Results For SO<sub>2</sub>/Salt Spray Tests

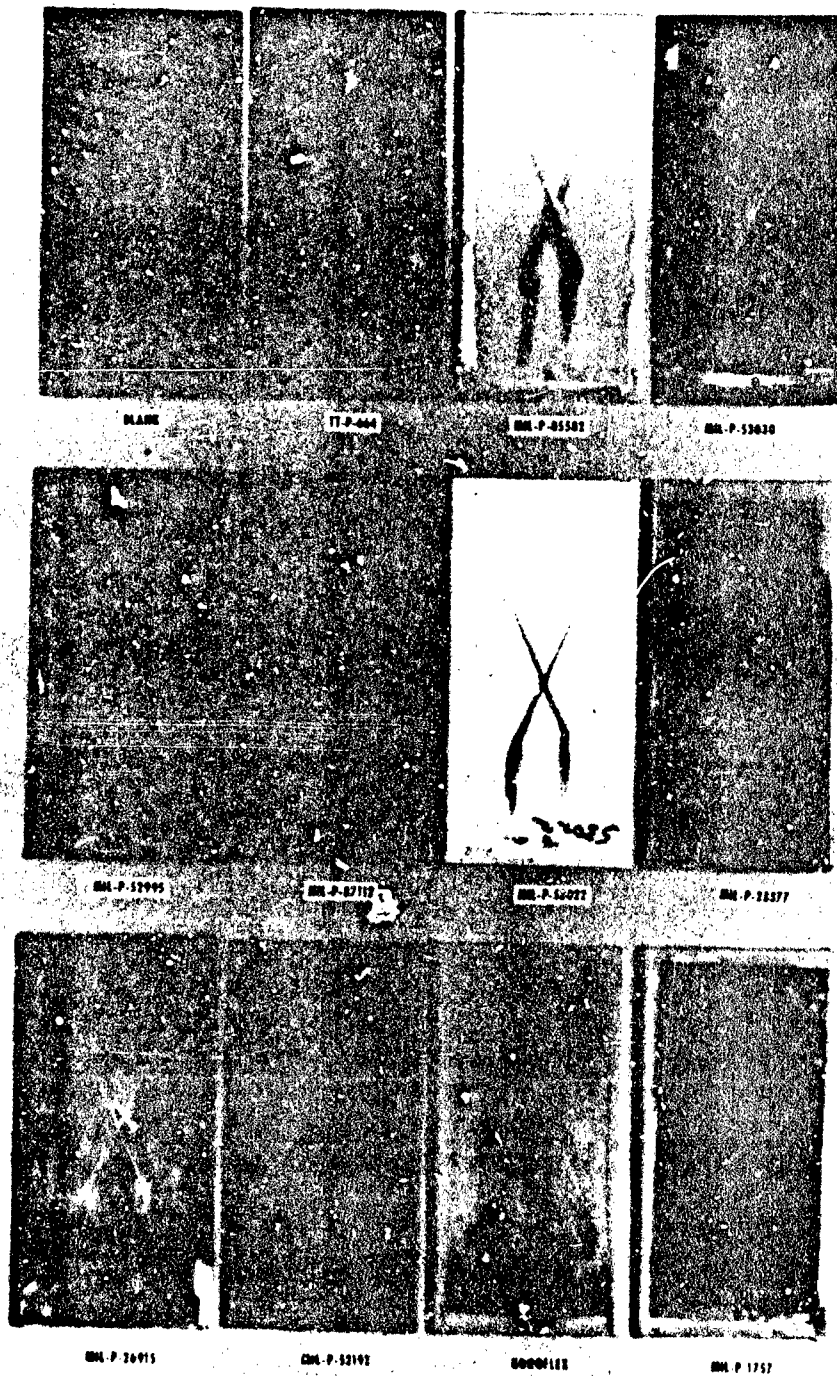


Figure 9. Steel Panel (Painted) From  $\text{SO}_2$ /Salt-Spray Test



NADC-85029-80

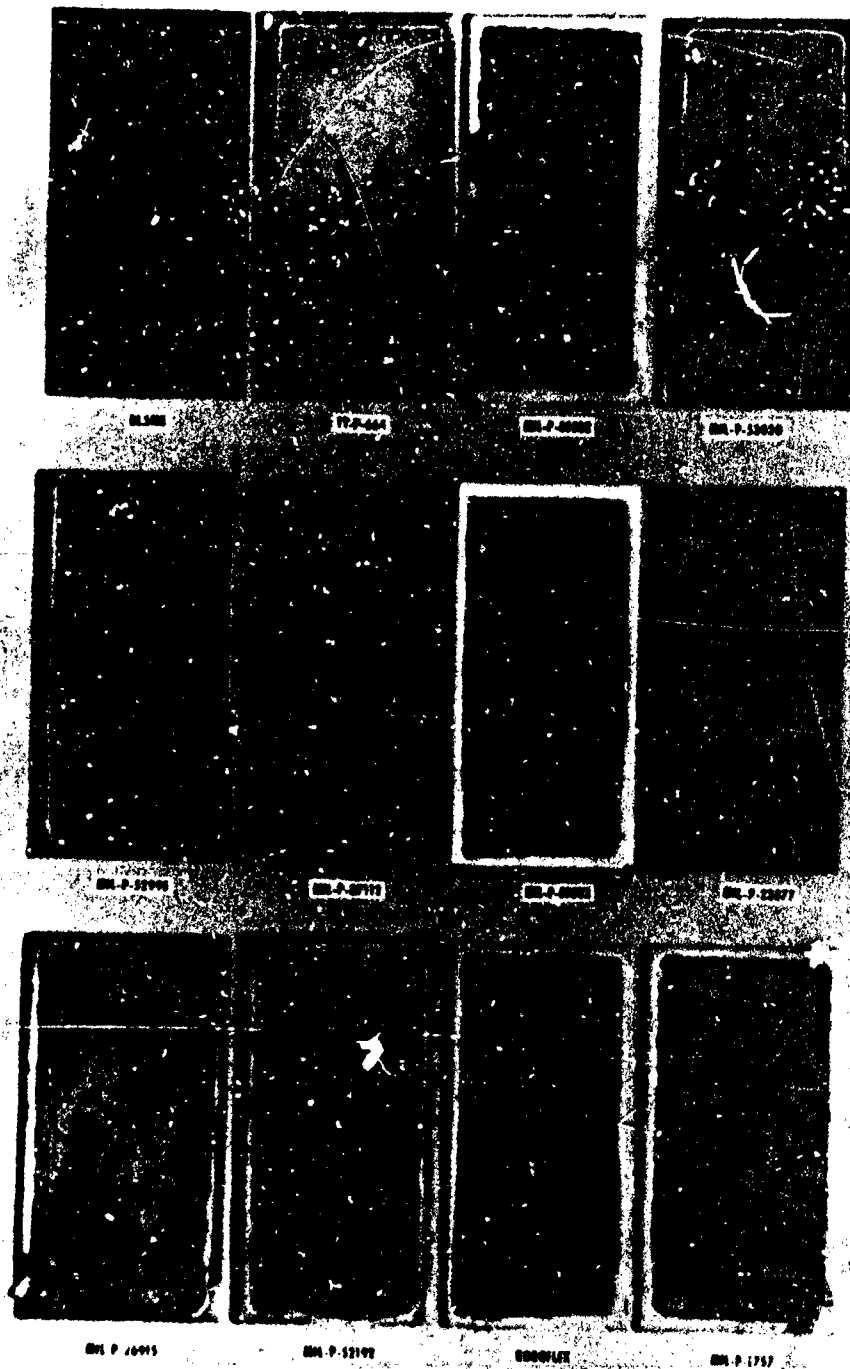


Figure 10. Steel Panels (Stripped) From SO<sub>2</sub>/Salt-Spray Test

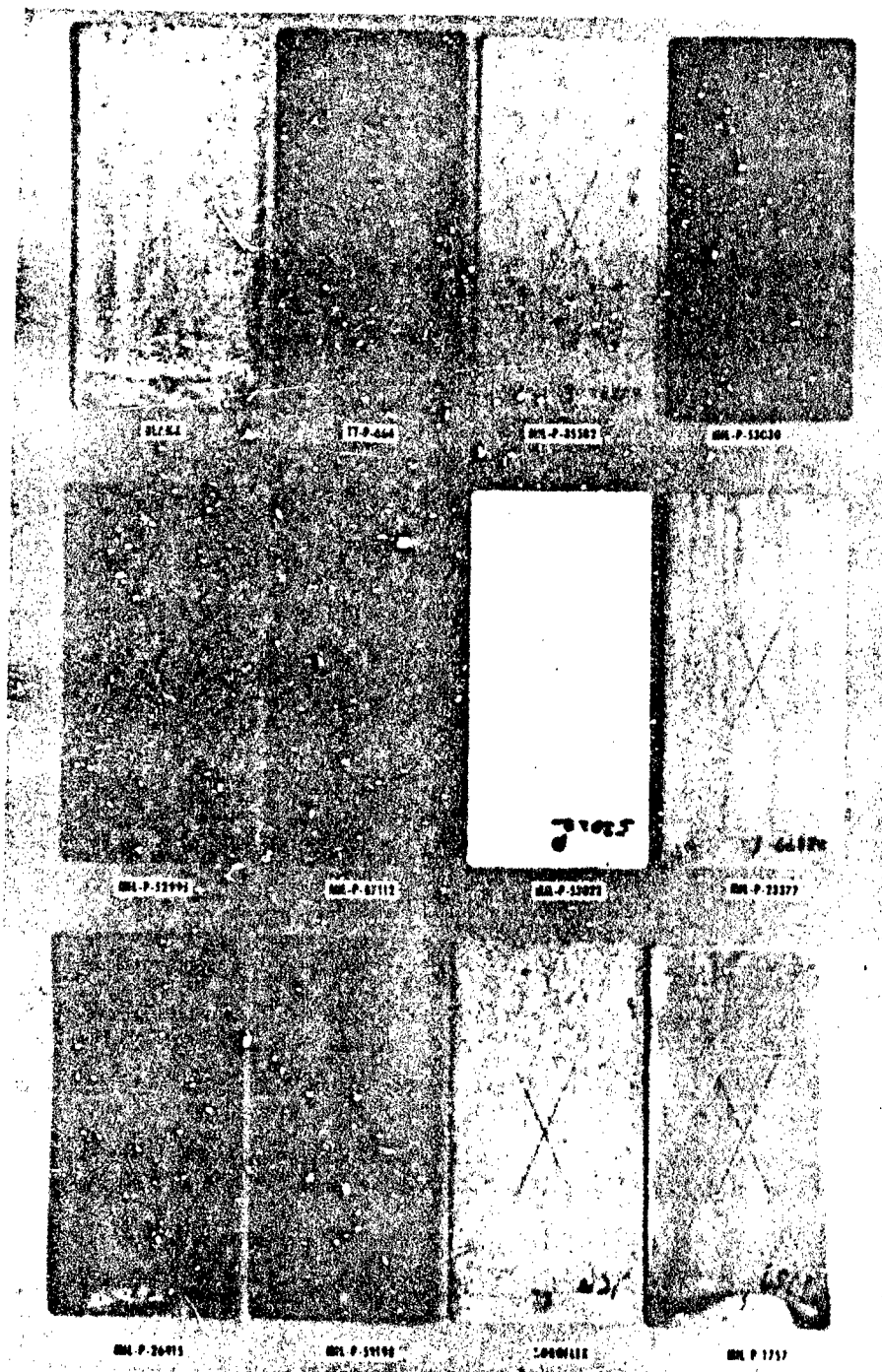


Figure 11. Aluminum Panels (Painted) From SO<sub>2</sub>/Salt-Spray Test

NADC-85029-60

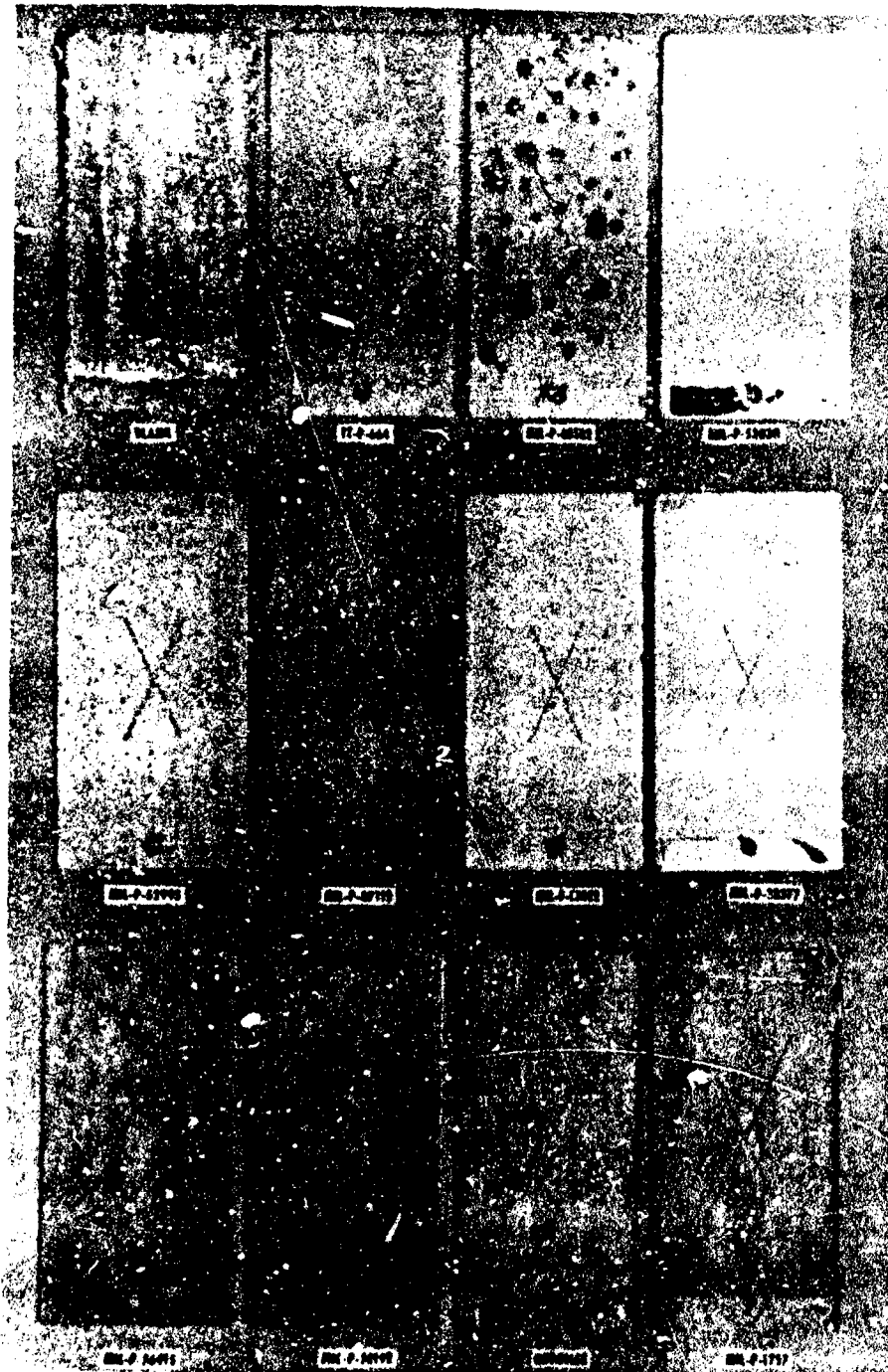
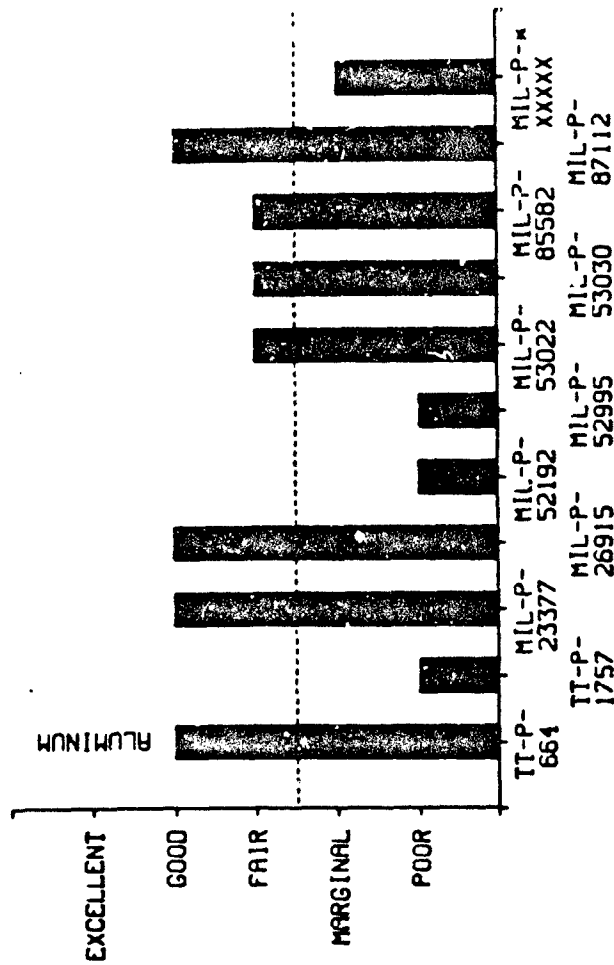


Figure 12. Aluminum Panels (Stripped) From SO<sub>2</sub>/Salt-Spray Test



- Excellent:** No corrosion in scribe, no filaments leading away from the scribe, and no corrosion on the rest of the panel.
- Good:** Slight corrosion in scribe filaments less than 1/16 inch leading away from the scribe, and no corrosion on the rest of the panel.
- Fair:** Corrosion in scribe, filaments less than 1/8 inch leading away from the scribe, no corrosion on the rest of the panel.
- Marginal:** Corrosion in scribe, filaments less than 1/8 inch leading away from the scribe and a few spots of corrosion on the rest of the panel.
- Poor:** Corrosion in scribe, filaments greater than 1/8 inch leading away from the scribe and/or more than a dozen spots of corrosion on the rest of the panel.

Figure 13. Results For The Filiform Corrosion Test

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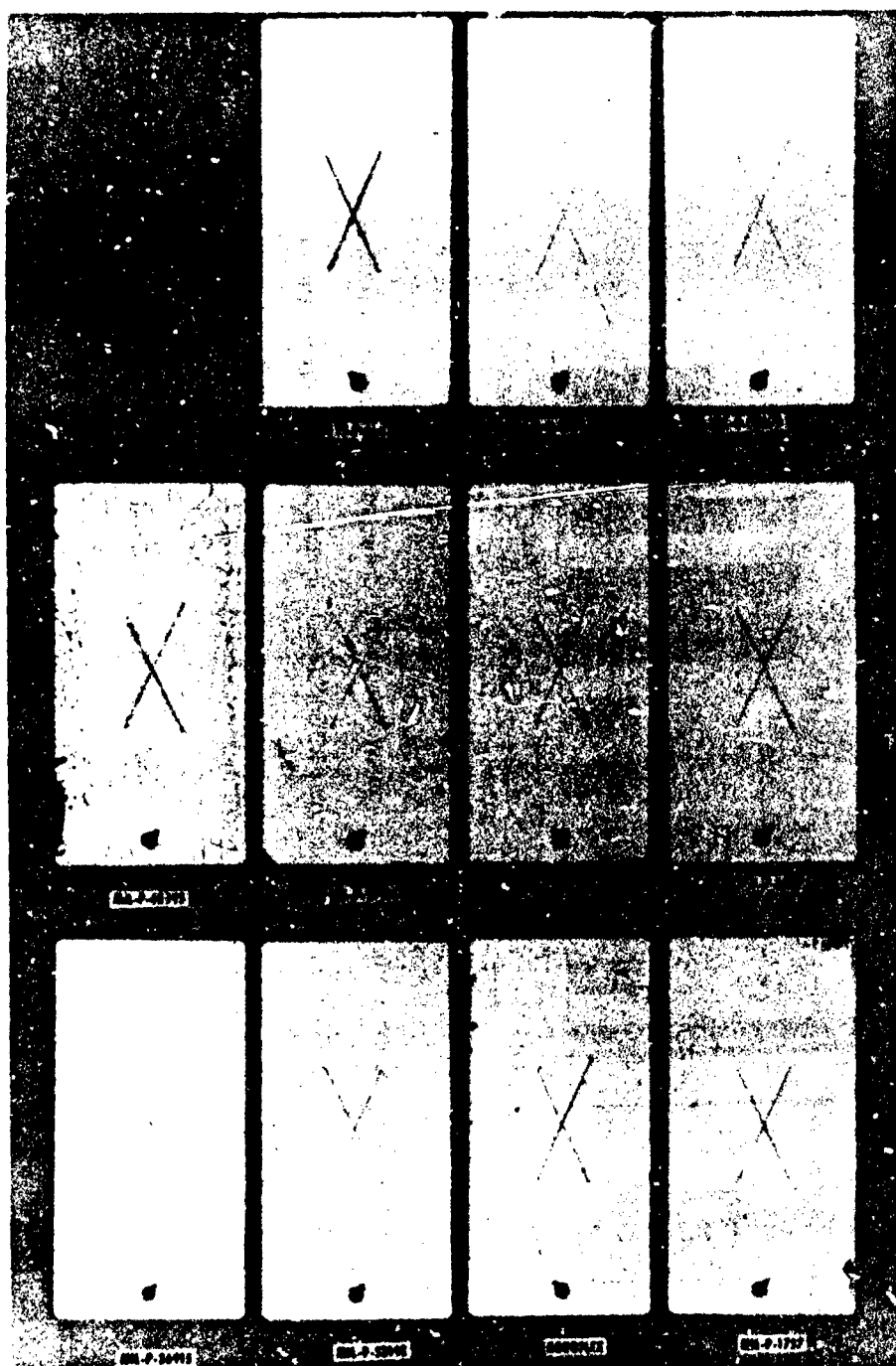


Figure 14. Aluminum Panels (Painted) From Filiform Corrosion Test

NADC-85029-60

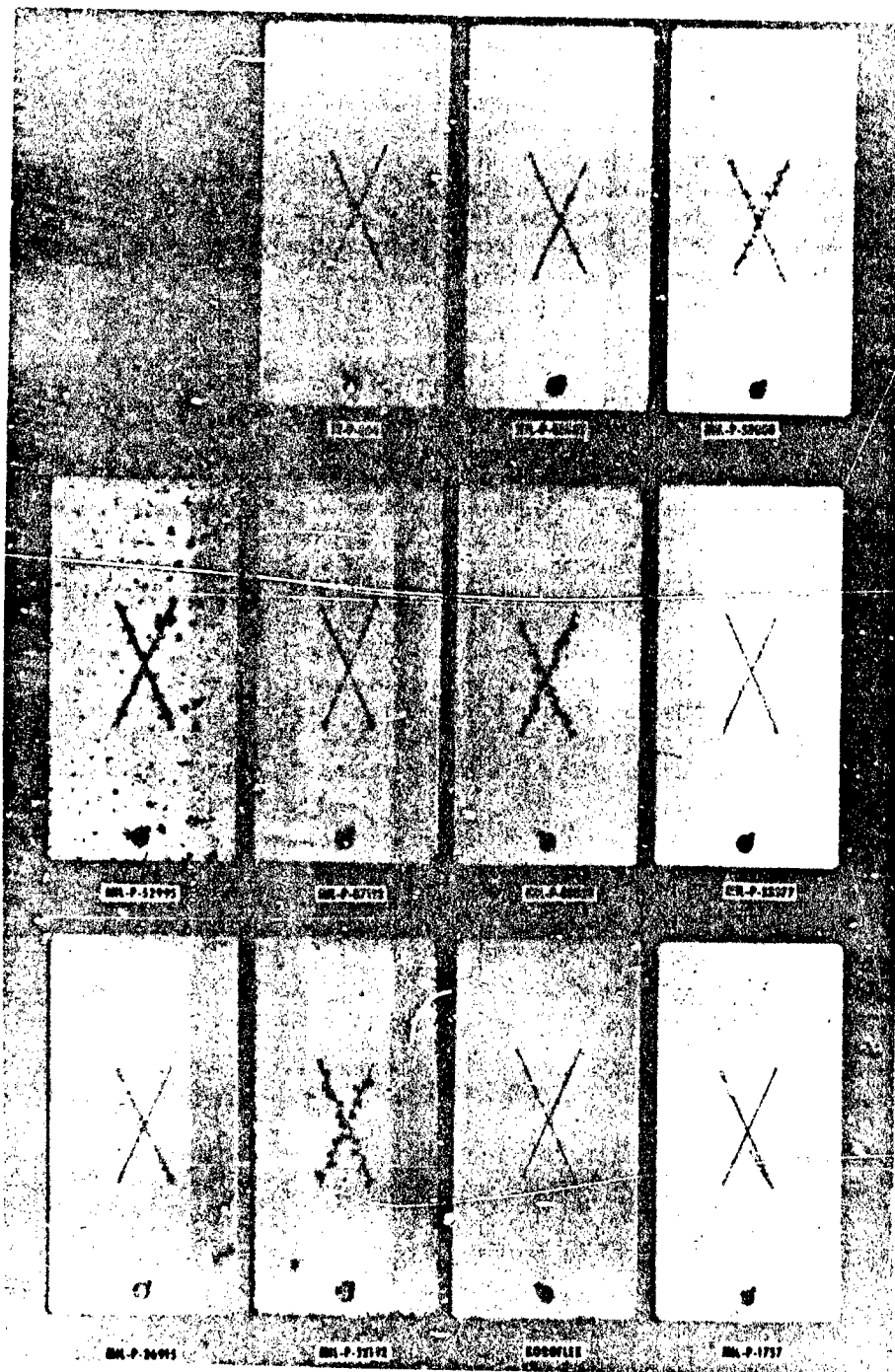


Figure 15. Aluminum Panels (Stripped) From Filiform Corrosion Test

Corrosion protection is one of the primary functions of a primer and is, therefore, a property of great importance when selecting a material for a particular application. This selection should be made only after considering the substrate to be protected and the surrounding environment. The application can vary from one piece of equipment to the next. Therefore, a material suited to the particular substrate should be used. Some materials perform better on steel, while others perform better on aluminum. In some cases, both substrates are present; and this requires a material that works well on both. In addition, the severity of the environment dictates the degree of protection that is required. These results are only an indication of the ability of these primers to prevent corrosion. There is little correlation between different corrosion tests, because of the unique conditions of each test. The SO<sub>2</sub>/salt-spray test is a better corrosion test for aircraft carrier environments or highly industrialized areas where stack exhaust gases are prevalent. The regular salt-spray test represents general conditions for corrosion. The filiform corrosion test covers highly humid and acidic environments where equipment could be susceptible to this type of corrosion.

### SUMMARY

The objective of this investigation was to evaluate various primers available for military equipment and provide comparative performance information to designers and engineers who specify and apply these materials. The eleven primers evaluated varied in performance from poor to excellent in corrosion protection, flexibility, adhesion, and chemical resistance. The corrosion resistance and adhesion varied between steel and aluminum substrates. In addition, these materials differed in composition (affecting not only physical properties but, also, application and cure).

Military equipment is constructed of various materials and is subjected to a wide variety of operational environments. The designer must consider these operational factors when specifying a coating system. He also must consider the application environment and scenario. The information provided in this report can then be used to determine the most effective primer for the intended use. By this process, equipment operational readiness and life-times can be increased.

### ACKNOWLEDGEMENT

The authors wish to acknowledge the efforts of Mr. William J. Green for his assistance in performing the tests in this study.

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